

A NEW FORMULATION OF THE MULTICOMPONENT TRANSPORT EQUATIONS
FOR USE IN LAMINAR BOUNDARY LAYER PROBLEMS

by

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This research was supported by the National
Aeronautics and Space Administration under
NASA Research Grant NGR 22-009-052

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May 1966

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ABSTRACT

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A new formulation of the multicomponent boundary layer problem which is convenient for numerical calculations is developed. This is accomplished by a modification of the usual Chapman-Enskog procedure which is intermediate between that procedure and Grad's thirteen-moment method. The relations which are developed do not involve transport coefficients but rather expressions for the gradients of the physical variables as linear combinations of the fluxes. The complete set of boundary layer equations turn out to be a set of first-order differential equations and a set of algebraic equations which are linear in the fluxes. These expressions contain the averaged cross sections instead of transport coefficients.

The method is extended to include chemically reacting mixtures of polyatomic molecules. It is shown that the method can be further extended to two temperature fluids when one of the species has a small mass and to mixtures where it is necessary to retain higher-order terms in the Chapman-Enskog procedure in evaluating the collision integration for some of the species.

The results are applied to the specific case of the stagnation point boundary layer.

I. INTRODUCTION

In order to solve boundary layer problems with many species present, numerical techniques must invariably be used. The thermal conductivity and diffusion coefficients appearing in the boundary layer equations are usually complicated functions of temperature and concentration.¹ In the cases where similarity solutions exist, one usually tries to reduce the governing equations to a set of first-order ordinary differential equations plus a set of algebraic equations.^{1,2} It is usual to neglect thermal diffusion in this procedure.¹

In this report we have attempted to formulate the boundary layer problem with many species present in a way that is convenient for numerical calculations. To accomplish this we have modified the usual Chapman-Enskog^{3,4} procedure for obtaining normal solutions to the Boltzmann equation for monotonic gases which is presented in Hirschfelder, Curtiss, and Bird³ (hereafter shortened to HCB). We begin (part II) with the linear integral equations for the first-order distributions function given in HCB, but instead of seeking solutions to these equations which are proportional to the gradients of the physical variables* as was done in HCB, we have chosen to start with a more general form of the solutions which we allowed to contain unknown vector function of the fluxes** and the physical variables (see eq. 2.7 and compare with eq. 7.3-29 of HCB). The first few of these undetermined vector functions were then evaluated by substituting the solutions into the definitions of the heat and mass fluxes for the individual species. The resulting expressions were then

* i.e., the temperature, pressure, concentration, etc.

** e.g., the heat flux moment of the distribution function

used to eliminate these functions from the solutions and thus to express the solutions in terms of the fluxes instead of the forces (i.e., the gradients of physical variables) as was done in HCB. The remaining arbitrary functions were then determined by substituting these expressions for the solutions into the linear integral equations given in HCB for the first-order distribution functions, then multiplying both sides of the resulting expressions by the Sonine polynomials of order $3/2$ and of arbitrary degrees and integrating to match the coefficients.*

After using the orthogonality relations for the Sonine polynomials, this led to a set of equations which determine the remaining unknown functions appearing in the solutions. The first few of these equations are expressions for the forces in terms of the fluxes. The remaining equations are merely algebraic expressions which determine the unknown functions appearing in the solutions. The important thing here is that the first few of these equations turn out to be of a form in which the gradients of the physical quantities are given explicitly as linear combinations of the fluxes instead of being the other way around as they are in the usual Chapman-Enskog procedure. It is felt that this form is more convenient for numerical calculations when applied to boundary layer problems than the usual relations in terms of transport properties.**

These equations were then truncated (part III) to give the usual first-order approximations in the polynomial expansions. The truncated system of equations was then rearranged and expressed in terms of the averaged cross sections. This procedure was used for the heat transfer

* i.e., by taking moments of the equation

** For example, compare equations (7.4-64) through (7.4-66) and equations (7.4-55) of HCB with equation (18.2) below.

and diffusion part of the solution. The shear stress was treated in almost the standard way, however, with only slight modification.

The method used here is essentially intermediate between Grad's moment method⁶ and the Chapman-Enskog procedure. A comparison of equations (4.7) through (4.21) with equations (3.8) and (7.2) through (7.5) of reference 6 shows that the form of the resulting equations is quite similar. The principal advantage of this method over the moment method is that the amount of manipulation necessary to derive the equations is considerably reduced. This is due to the fact that we expanded Boltzmann's equation in a uniformity parameter (the ratio of the mean free path to a characteristic macroscopic length) before any moments were taken. This resulted in a simpler set of equations which had to be carried through the calculations. Since the method is closer to the Chapman-Enskog procedure than the 13 moment method, it is easier to take over results which have been tabulated or carried out within the framework of that procedure which has been extensively studied.

The method has additional advantages. It can be easily extended to two temperature fluids and to higher order (in the polynomial expansions) for certain individual components while only retaining the lower order terms for all the other components. This is useful when electrons are present.⁷

In order to test the method we have used the results obtained in this report to calculate the thermal conductivity of a single-component gas and the binary diffusion coefficient of a two-component isothermal mixture (see Appendix B). These were in agreement with those given in HCB.

In Appendix C we have brought in the Eucken correction so that the results could be extended to polyatomic gases. This was accomplished by comparing the results obtained here with those of reference 11 and then noticing that it was necessary to add a term to the expression for the heat flux in order to make them agree.

Finally in Part IV these results were applied to the formulation of the general boundary layer problem of a mixture of reacting gases. These results of Part III were extended to gases with internal motion and chemical reactions in the usual way. The boundary layer equations are written as a set of first-order differential equations plus a set of algebraic equations which are linear in the fluxes. These equations are in a more convenient form for numerical calculations than those which would be obtained by using transport coefficients. The specific case of the stagnation point boundary layer was treated in detail.

Many of the results used below are taken over directly from HCB. When this has been done their notation has been used without explanation, but the relevant equation numbers are given.

II. GENERAL FORMULATION

In this section we develop an "exact" solution to the linearized Boltzmann equation for a multi-component mixture. The solution is in such a form that the forces (i.e., gradient of the properties) are expressed as a linear combination of the fluxes.

We begin with equation (7.3-26) of HCB¹ for the perturbation function ϕ_i which is:

$$\begin{aligned} f_i^{(0)} \left[\frac{n}{n_i} (\underline{v}_i \cdot \underline{a}_i) + (\underline{b}_i : \frac{\partial}{\partial \underline{r}} \underline{v}_0) - (\frac{5}{2} - w_i^2) (\underline{v}_i \cdot \frac{\partial \ln T}{\partial \underline{r}}) \right] \\ = \sum_j \iint f_i^{(0)} f_j^{(0)} (\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} \, d\mathbf{b} \, d\mathbf{b}' \, d\underline{v}_j \end{aligned} \quad (2.1)$$

where the ϕ_i 's are related to the perturbation in f_i by

$$f_i^{(1)} = f_i^{(0)} \phi_i \quad (2.2)$$

If we define θ_i by:

$$\theta_i \equiv \phi_i - \underline{B}_i : \frac{\partial}{\partial \underline{r}} \underline{v}_0 \quad (2.3)$$

The equation for θ_i must be:*

$$\begin{aligned} \frac{n}{n_i} \underline{a}_i \cdot f_i^{(0)} \underline{v}_i - \frac{\partial \ln T}{\partial \underline{r}} \cdot f_i^{(0)} \underline{v}_i (\frac{5}{2} - w_i^2) = \\ = \sum_j \iint f_i^{(0)} f_j^{(0)} (\theta_i' + \theta_j' - \theta_i - \theta_j) g_{ij} \, d\mathbf{b} \, d\mathbf{b}' \, d\underline{v}_j \end{aligned} \quad (2.4)$$

* See HCB p. 469 for details. $(f_i^{(0)})$ is the Maxwellian distribution function for species i and $\underline{w}_i \equiv \sqrt{\frac{m_i}{2kT}} \underline{v}_i$

Multiplying both sides of this equation by $\underline{w}_i S^r(w_i^2)$ (where $S^r(w_i^2)$ is the r 'th Sonine Polynomial of order $3/2$ and argument w_i^2)* and integrating with respect to \underline{v}_i , we get:

$$\begin{aligned} & \frac{n}{n_i} \underline{d}_i \cdot \int f_i^{(0)} \underline{v}_i \underline{w}_i S^r(w_i^2) d\underline{v}_i - \frac{\partial \ln T}{\partial \underline{r}} \cdot \int f_i^{(0)} \underline{v}_i \underline{w}_i \left(\frac{5}{2} - w_i^2\right) S^r(w_i^2) d\underline{v}_i \\ &= \frac{n}{n_i} \frac{1}{3} \left(\sqrt{\frac{m_i}{2kT}} \underline{d}_i \int f_i^{(0)} \underline{v}_i^2 S^r(w_i^2) d\underline{v}_i - \frac{1}{3} \left(\frac{2kT}{m_i}\right)^2 \frac{\partial \ln T}{\partial \underline{r}} \int f_i^{(0)} w_i^2 S^1 S^r d\underline{w}_i \right) \quad (2.5) \\ &= \sum_j \left(\underline{w}_i S^r(w_i^2) \right) \iiint f_i^{(0)} f_j^{(0)} (\theta_i' + \theta_j' - \theta_i - \theta_j) g_{ij} b db d\epsilon d\underline{v}_j d\underline{v}_i \end{aligned}$$

where we have used equation 4 of section 1.42 of Chapman and Cowling⁴ and definition (7.2-11) of HCB to get the last relation.

Finally by using the relations (7.3-58) and (7.3-59) of HCB (i.e., the orthogonality relations for the Sonine Polynomials), we arrive at:

$$\begin{aligned} & \sqrt{\frac{2kT}{m_i}} \left\{ \frac{n}{2} \underline{d}_i \delta_{r0} - \frac{5}{4} n_i \frac{\partial \ln T}{\partial \underline{r}} \delta_{r1} \right\} = \quad (2.6) \\ & \sum_j \iiint f_i^{(0)} f_j^{(0)} \underline{w}_i S^r(w_i^2) (\theta_i' + \theta_j' - \theta_i - \theta_j) g_{ij} b db d\epsilon d\underline{v}_i d\underline{v}_j \end{aligned}$$

where δ_{rn} is the kronecker delta. Examination of equation (2.3) and of equations (7.3-29), (7.3-35), (7.3-26), and (7.3-61) of HCB shows that the θ_i must be of the form:

$$\theta_i = \underline{w}_i \cdot \sum_{n=0}^{\infty} \underline{a}_i^n S^n(w_i^2) \quad (2.7)$$

*Note that S^r is designated by $S_{3/2}^r$ in HCB.

where α_i^n is independent of \underline{W}_i .

From equation (2.3) and equations (7.3-29), (7.4-1), and (7.4-2) of HCB, it follows that:

$$n_i \bar{\underline{V}}_i = \int \underline{V}_i \varrho_i f_i^{(0)} d\underline{V}_i \quad (2.8)$$

Substituting eq. (2.7) in eq. (2.8), we get:

$$n_i \bar{\underline{V}}_i = \sum_{n=0}^{\infty} \alpha_i^n \cdot \int \underline{W}_i \underline{V}_i f_i^{(0)} S^n(W_i^2) d\underline{V}_i$$

From equation (4.2) of section 1.42 of Chapman and Cowling and definition (7.2-11) of HCB, we get:

$$n_i \bar{\underline{V}}_i = \frac{1}{3} \sqrt{\frac{m_i}{2kT}} \sum_n \alpha_i^n \int \underline{V}_i^2 S^n(W_i^2) f_i^{(0)} d\underline{V}_i,$$

and finally from equation (7.3-59) of HCB, we get*

$$n_i \bar{\underline{V}}_i = n_i \alpha_i^0 \sqrt{\frac{2kT}{m_i}} \cdot \frac{1}{2}$$

or

$$\alpha_i^0 = 2 \bar{\underline{W}}_i \quad (2.9)$$

Now the part of the translational heat flux vector due to the i'th species, \underline{q}_i , is given by:

$$\underline{q}_i = \frac{1}{2} m_i \int \underline{V}_i^2 \underline{V}_i f_i d\underline{V}_i \quad (2.10)$$

while the total heat flux vector \underline{q} is:

* i.e., We have used the orthogonality relations for the Sonine polynomials.

$$\underline{q} = \sum_i q_i \quad (2.11)$$

We now have:

$$\begin{aligned} q_i &= \frac{1}{2} m_i \int v_i^2 v_i f_i^{(0)} \theta_i dv_i \\ &= \frac{1}{2} m_i \left(\frac{2kT}{m_i} \right)^3 \int w_i^2 w_i f_i^{(0)} \theta_i dw_i \\ &= \frac{5}{4} m_i \left(\frac{2kT}{m_i} \right)^3 \int w_i f_i^{(0)} \theta_i dw_i - \\ &\quad - \frac{1}{2} m_i \left(\frac{2kT}{m_i} \right)^3 \int w_i f_i^{(0)} \left(\frac{5}{2} - w_i^2 \right) \theta_i dw_i \\ &= \frac{5}{4} m_i \left(\frac{2kT}{m_i} \right) \int v_i f_i^{(0)} \theta_i dv_i \\ &\quad - \frac{1}{3} \cdot \frac{1}{2} m_i \left(\frac{2kT}{m_i} \right)^3 \sum_n \mathcal{L}_i^n \int w_i^2 f_i^{(0)} S^1(w_i^2) S^n(w_i^2) dw_i \end{aligned}$$

Finally using equation (2.8) and equation (7.3-58) of HCB, we get:

$$q_i = \frac{5}{2} n_i kT \left[\bar{v}_i - \frac{1}{2} \left(\frac{2kT}{m_i} \right)^{1/2} \mathcal{L}_i^1 \right] \quad (2.12)$$

We now notice that since θ_i (as given by eq. 2.7) is an odd function of w_i , the auxiliary condition given by (7.3-18) and (7.3-20) in HCB are identically satisfied, and the auxiliary condition (7.3-19) is, by equation (2.9), equivalent to the condition:

$$\sum_i n_i m_i \bar{v}_i = 0 \quad (2.13)$$

After substituting equation (2.7) into equation (2.6), we arrive at

$$\sqrt{\frac{2kT}{m_i}} \left\{ \frac{1}{2} \frac{n}{n_i} d_i \delta_{ro} - \frac{5}{4} \frac{\partial \ln T}{\partial r} \delta_{rl} \right\} =$$

$$= - \sum_j \sum_n n_j \left\{ I_{ij}^{(r n)} \left(\begin{smallmatrix} r & n \\ i & i \end{smallmatrix} \right) \cdot \mathcal{Q}_i^n + I_{ij}^{(r n)} \left(\begin{smallmatrix} r & n \\ i & j \end{smallmatrix} \right) \cdot \mathcal{Q}_j^n \right\} \quad (2.14)$$

where

$$I_{ij}^{(r n)} \left(\begin{smallmatrix} r & n \\ s & k \end{smallmatrix} \right) = \frac{-1}{n_i n_j} \iiint f_i^{(0)} f_j^{(0)} S^r(w_s^2) w_s \left[S^n(w_k'^2) w_k' - S^n(w_k^2) w_k \right] \cdot$$

$$\cdot g_{ij} \, b \, db \, d\epsilon \, dv_i \, dv_j \quad (2.15)$$

In Appendix (A) we have shown that

$$I_{ij}^{(r n)} \left(\begin{smallmatrix} r & n \\ i & j \end{smallmatrix} \right) = \frac{1}{3} \underline{\underline{U}} \left[S^r(w_i^2) w_i, S^n(w_j^2) w_j \right]_{ij} \quad (2.16)$$

$$I_{ij}^{(r n)} \left(\begin{smallmatrix} r & n \\ i & i \end{smallmatrix} \right) = \frac{1}{3} \underline{\underline{U}} \left[S^r(w_i^2) w_i, S^n(w_i^2) w_i \right]_{ij} \quad (2.17)$$

Where $\underline{\underline{U}}$ is the unit tensor, the terms multiplying $\frac{1}{3} \underline{\underline{U}}$ on the right-hand side of equations (2.16) and (2.17) are defined in Chapman and Cowling section 4.4 by equations (4), (5), and (9) or more specifically by (1) in section 9.3.

Substituting equations (2.16), and (2.17) into equation (2.14) yields:

$$6kT \left\{ \frac{1}{2} \frac{n}{n_i} d_i \delta_{ro} - \frac{5}{4} \frac{\partial \ln T}{\partial r} \delta_{rl} \right\} =$$

$$= - \sum_j \sum_n m_i n_j \sqrt{\frac{2kT}{m_i}} \mathcal{Q}_i^n \left[S^r(w_i^2) w_i, S^n(w_i^2) w_i \right]_{ij}$$

$$- \sum_j \sum_n \sqrt{m_i m_j} n_j \sqrt{\frac{2kT}{m_j}} \mathcal{Q}_j^n \left[S^r(w_i^2) w_i, S^n(w_j^2) w_j \right]_{ij} \quad (2.18)$$

Equations (2.18) constitute a J-fold infinite set of equations where J is the number of species in the mixture. These determine the $J \times \infty$ constants α_i^n . It should be noted that these are vector equations since the α_i^n are vectors; therefore, there is actually a 3-J fold infinity of scalar equations. Equations (2.9), (2.11), and (2.12) relate the first two of the α_i^n to the fluxes, and equation (2.13) adds an additional restriction on the α_i^n 's.

The α_i^n 's of equations (2.18) are flux-like quantities. In fact the α_i^0 's are the mass fluxes, and the α_i^1 's are the conduction heat fluxes of the individual species. The terms on the left side of these equations are the forces (or potential gradients). These equations are in the form of a set of first-order differential equations plus a set of linear algebraic equations with all the derivatives appearing on the left-hand side.

III. FIRST-ORDER APPROXIMATION

In this section we shall truncate the infinite set of equations (2.18) and proceed to rearrange and simplify the results. The equations finally obtained are written down in terms of average cross sections ($\Omega_{kj}^{(k,l)}$ in HCB's notation) which are tabulated for various molecular potentials.

A comparison of this formulation of the problem (equation (2.18) with that of HCB shows that it is necessary to retain the terms involving α_i^0 and α_i^1 in order to get the usual first approximation for all transport coefficients.* We therefore retain only these terms, and we are left with a set of $2 \times J$ equations (2.18) which are:

$$\begin{aligned}
 3kT \frac{n}{n_i} \underline{d}_i = & - 2 \sum_j n_j \underline{m}_i \bar{v}_i [\underline{w}_i, \underline{w}_i]_{ij} \\
 & - 2 \sum_j \sqrt{\underline{m}_i \underline{m}_j} n_j \bar{v}_j [\underline{w}_i, \underline{w}_j]_{ij} - \\
 & - \sum_j \underline{m}_i^2 n_j \chi_i [\underline{w}_i, s^1(\underline{w}_i^2) \underline{w}_i]_{ij} \\
 & - \sum_j \underline{m}_j \sqrt{\underline{m}_i \underline{m}_j} n_j \chi_j [\underline{w}_i, s^1(\underline{w}_j^2) \underline{w}_j]_{ij}
 \end{aligned} \tag{3.1}$$

$$\begin{aligned}
 \frac{15}{2} kT \frac{\partial \ln T}{\partial x} = & 2 \sum_j n_j \underline{m}_i \bar{v}_i [s^1(\underline{w}_i^2) \underline{w}_i, \underline{w}_i]_{ij} \\
 & + 2 \sum_j \sqrt{\underline{m}_i \underline{m}_j} n_j \bar{v}_j [s^1(\underline{w}_i^2) \underline{w}_i, \underline{w}_j]_{ij} \\
 & + \sum_j \underline{m}_i^2 n_j \chi_i [s^1(\underline{w}_i^2) \underline{w}_i, s^1(\underline{w}_i^2) \underline{w}_i]_{ij} \\
 & + \sum_j \sqrt{\underline{m}_i \underline{m}_j} \underline{m}_j n_j \chi_j [s^1(\underline{w}_i^2) \underline{w}_i, s^1(\underline{w}_i^2) \underline{w}_i]_{ij}
 \end{aligned} \tag{3.2}$$

*To this approximation all cross coupling effects such as thermal diffusion are retained. This approximation usually gives the transport coefficients quite accurately.

Where we have used eq. (2.9) to eliminate $\underline{\alpha}_i^0$, and we have introduced the quantity $\underline{\chi}_i$ defined by

$$\underline{\chi}_i \equiv \frac{1}{m_i} \sqrt{\frac{2kT}{m_i}} \underline{\alpha}_i^1 \quad (3.3)$$

Using equations (7.A-1) through (7.A-9) of HCB in equations (3.1) and (3.2), we get

$$\begin{aligned} \frac{n}{n_i} \underline{d}_i = & \frac{8}{3kT} \sum_j n_j (\underline{\chi}_i - \underline{\chi}_j) \mu_{ij}^2 (\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)}) \\ & - \frac{16}{3kT} \sum_j n_j (\bar{v}_i - \bar{v}_j) \mu_{ij} \Omega_{ij}^{(1,1)} \end{aligned} \quad (3.4)$$

$$\begin{aligned} \frac{15}{16} m_i kT \frac{\partial \ln T}{\partial \underline{r}} = & - 2 \sum_j n_j (\bar{v}_i - \bar{v}_j) \mu_{ij}^2 (\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)}) \\ & + \sum_j n_j (\underline{\chi}_i - \underline{\chi}_j) \mu_{ij}^3 \left\{ (\Omega_{ij}^{(1,3)} - \frac{5}{2} \Omega_{ij}^{(1,2)}) - \frac{5}{2} (\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)}) \right\} \\ & + 2 \sum_j n_j (m_i \underline{\chi}_i + m_j \underline{\chi}_j) \left(\frac{m_i}{m_i + m_j} \right) \mu_{ij}^2 \Omega_{ij}^{(2,2)} + \\ & + \frac{15}{2} \sum_j n_j (m_i^2 \underline{\chi}_i - m_j^2 \underline{\chi}_j) \left(\frac{m_i}{m_i + m_j} \right)^2 \mu_{ij} \Omega_{ij}^{(1,1)}. \end{aligned} \quad (3.5)$$

Where μ_{ij} is the reduced mass defined by

$$\frac{1}{\mu_{ij}} = \frac{1}{m_i} + \frac{1}{m_j}, \quad (3.6)$$

the set of equations (3.5) all contain a temperature gradient on the left-hand side. Since, however, algebraic equations are more convenient than

differential equations, it will be convenient to replace equations (3.5) by a single differential equation plus a set of linear algebraic equations. In order to accomplish this we proceed as follows:

Multiplying equation (3.5) by n_i and summing on i , we get upon noting that $\Omega_{ij}^{(\ell,k)} = \Omega_{ji}^{(\ell,k)}$ and $\mu_{ij} = \mu_{ji}$

$$\begin{aligned} \frac{15}{16} \rho_{KT} \frac{\partial \ln T}{\partial r} = & 2 \sum_i \sum_j n_i n_j (m_i \chi_i + m_j \chi_j) \left(\frac{m_i}{m_i + m_j} \right) \mu_{ij}^2 \Omega_{ij}^{(2,2)} \\ & + \frac{15}{2} \sum_i \sum_j n_i n_j (m_i^2 \chi_i - m_j^2 \chi_j) \left[\frac{m_i^2}{(m_i + m_j)^2} \right] \mu_{ij} \Omega_{ij}^{(1,1)} \end{aligned}$$

or

$$\begin{aligned} \frac{15}{16} \rho_{KT} \frac{\partial \ln T}{\partial r} = & 2 \sum_i \sum_j n_i m_i \chi_i n_j \mu_{ij} \left[\mu_{ij} \Omega_{ij}^{(2,2)} + \frac{15}{4} m_i \left(\frac{m_i - m_j}{m_i + m_j} \right) \Omega_{ij}^{(1,1)} \right] \quad (3.7) \end{aligned}$$

where the density ρ is given by

$$\rho = \sum_i n_i m_i \quad (3.8)$$

Eliminating $\frac{15}{16} \rho_{KT} \frac{\partial \ln T}{\partial r}$ between equations (3.7) and (3.5), we get

$$\begin{aligned} 2 \sum_j n_j (\bar{v}_i - \bar{v}_j) \mu_{ij}^2 (\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)}) = & \\ \sum_j n_j (\chi_i - \chi_j) \mu_{ij}^3 \left\{ (\Omega_{ij}^{(1,3)} - \frac{5}{2} \Omega_{ij}^{(1,2)}) - \frac{5}{2} (\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)}) \right\} \end{aligned}$$

$$\begin{aligned}
 & + \frac{15}{2} \sum_j n_j (m_i^2 \zeta_i - m_j^2 \zeta_j) \left(\frac{m_i}{m_i + m_j} \right)^2 \mu_{ij} \Omega_{ij}^{(1,1)} \\
 & + 2 \sum_j n_j (m_i \zeta_i + m_j \zeta_j) \left(\frac{m_i}{m_i + m_j} \right) \mu_{ij}^2 \Omega_{ij}^{(2,2)} \\
 & - \frac{m_i}{\rho} \frac{15}{2} \sum_j n_j m_j^2 \zeta_j \sum_l n_l \left(\frac{m_j - m_l}{m_j + m_l} \right) \mu_{jl} \Omega_{jl}^{(1,1)} \\
 & - \frac{2m_i}{\rho} \sum_j n_j m_j \zeta_j \sum_l n_l \mu_{jl}^2 \Omega_{jl}^{(2,2)}
 \end{aligned}$$

By multiplying both sides of this equation by n_i and using the Kronecker delta, we get after introducing different dummy indices:

$$\begin{aligned}
 & \sum_j \bar{y}_j^2 \sum_l n_j n_l (\delta_{ji} - \delta_{li}) \mu_{lj}^2 (\Omega_{jl}^{(1,2)} - \frac{5}{2} \Omega_{jl}^{(1,1)}) \\
 & = \sum_j \zeta_j^2 m_j \sum_l n_j n_l \left\{ \frac{\delta_{ji} m_j + \delta_{il} m_l}{m_j + m_l} - \frac{n_i m_i}{\rho} \right\} \mu_{jl}^2 \Omega_{jl}^{(2,2)} \\
 & + \sum_j \zeta_j \frac{15}{2} m_j^2 \sum_l n_j n_l \left\{ \frac{\delta_{ji} m_j^2 - \delta_{il} m_l^2}{(m_j + m_l)^2} - \left(\frac{m_j - m_l}{m_j + m_l} \right) \frac{n_i m_i}{\rho} \right\} \mu_{jl} \Omega_{jl}^{(1,1)} \\
 & + \sum_j \zeta_j \sum_l n_j n_l (\delta_{ji} - \delta_{il}) \mu_{jl}^3 \left\{ (\Omega_{jl}^{(1,3)} - \frac{5}{2} \Omega_{jl}^{(1,2)}) - \frac{5}{2} (\Omega_{jl}^{(1,2)} - \frac{5}{2} \Omega_{jl}^{(1,1)}) \right\}
 \end{aligned}$$

Introducing the mass flux of the i 'th species j_i defined by

$$j_i = n_i m_i \bar{v}_i \quad (3.9)$$

the mass fraction of the i 'th species c_i defined by

$$c_i = n_i m_i / \rho \quad (3.10)$$

and \mathcal{F}_i defined by

$$\mathcal{F}_i \equiv n_i m_i^2 \mathcal{F}_i = n_i m_i \sqrt{\frac{2kT}{m_i}} \mathcal{F}_i^1 \quad (3.11)$$

We have:

$$\begin{aligned} & \sum_j \mathcal{F}_j^2 \sum_{\ell} c_{\ell} (\delta_{ji} - \delta_{\ell i}) \left[\frac{\mu_{j\ell}}{(m_j + m_{\ell})} \right] (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)}) \\ &= \sum_j \mathcal{F}_j^2 \sum_{\ell} c_{\ell} \left\{ \frac{\delta_{ji} m_j + \delta_{i\ell} m_{\ell} - c_i (m_j + m_{\ell})}{(m_j + m_{\ell})} \right\} \left[\frac{\mu_{j\ell}}{(m_j + m_{\ell})} \right] \Omega_{j\ell}^{(2,2)} \\ &+ \sum_j \mathcal{F}_j^2 \frac{15}{2} \sum_{\ell} c_{\ell} \left\{ \frac{\delta_{ji} m_j^2 - \delta_{i\ell} m_{\ell}^2 - c_i (m_j^2 - m_{\ell}^2)}{(m_j + m_{\ell})^2} \right\} \left[\frac{m_j}{m_j + m_{\ell}} \right] \Omega_j^{(1,1)} \\ &+ \sum_j \mathcal{F}_j \sum_{\ell} c_{\ell} (\delta_{ji} - \delta_{i\ell}) \left[\frac{m_{\ell} \mu_{j\ell}}{(m_j + m_{\ell})^2} \right] \left\{ \Omega_{j\ell}^{(1,3)} - \frac{5}{2} \Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)} \right\} \end{aligned} \quad (3.12)$$

Equation (3.4) can now be written as:

$$\begin{aligned} \frac{m_i n}{\rho} \mathcal{d}_i &= \frac{8}{3kT} \sum_j \mathcal{F}_j \sum_{\ell} c_{\ell} \left(\frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i}}{m_{\ell} + m_j} \right) \left(\frac{m_{\ell}}{m_{\ell} + m_j} \right) (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{\ell j}^{(1,1)}) \\ &- \frac{16}{3kT} \sum_j \mathcal{F}_j \sum_{\ell} c_{\ell} \left(\frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i}}{m_{\ell} + m_j} \right) \Omega_{\ell j}^{(1,1)}. \end{aligned} \quad (3.13)$$

It will be convenient to introduce d_i^* defined by:

$$d_i^* \equiv \frac{n}{\rho} \left\{ m_i \mathcal{d}_i - c_i \sum_j m_j \mathcal{d}_j \right\}, \quad (3.14)$$

and we have from equation (3.13)

$$d_i^* = \frac{8}{3kT} \sum_j \sum_{\ell} c_{\ell} \left\{ \frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i} - c_i(m_j - m_{\ell})}{m_{\ell} + m_j} \right\} \left(\frac{m_{\ell}}{m_{\ell} + m_j} \right) (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)})$$

$$- \frac{16}{3kT} \sum_j \sum_{\ell} c_{\ell} \left\{ \frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i} - c_i(m_j - m_{\ell})}{m_{\ell} + m_j} \right\} \Omega_{j\ell}^{(1,1)} \quad (3.15)$$

Equation (3.7) can now be written as:

$$\frac{\partial \ln T}{\partial \underline{r}} = \frac{32}{15 kT} \sum_j \sum_{\ell} c_{\ell} \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) \left[\Omega_{j\ell}^{(2,2)} + \frac{15}{4} \left(\frac{m_j - m_{\ell}}{m_{\ell}} \right) \Omega_{j\ell}^{(1,1)} \right] \quad (3.16)$$

From equation (2.11), (2.12), (3.9), and (3.10), we have

$$\underline{q} = \sum_j \left(\frac{5}{2} \frac{kT}{m_j} \right) \underline{j}_j - \frac{5}{4} kT \sum_j \frac{1}{m_j} \underline{f}_j, \quad (3.17)$$

and from equations (2.13) and (3.9) we get

$$\sum_j \underline{j}_j = 0 \quad (3.18)$$

It is now convenient to define the following quantities

$$A_{ij} \equiv \frac{2}{3kT} \sum_{\ell} c_{\ell} (\delta_{ji} - \delta_{\ell i}) \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)}) \quad (3.19)$$

$$B_{ij} \equiv \frac{2}{3kT} \sum_{\ell} c_{\ell} \left\{ \frac{\delta_{ji} m_j + \delta_{i\ell} m_{\ell} - c_i(m_j + m_{\ell})}{m_j + m_{\ell}} \right\} \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) \Omega_{j\ell}^{(2,2)}$$

$$+ \frac{5}{2kT} \sum_{\ell} c_{\ell} \left\{ \frac{\delta_{ji} m_j^2 - \delta_{i\ell} m_{\ell}^2 - c_i(m_j^2 - m_{\ell}^2)}{(m_j + m_{\ell})^2} \right\} \left(\frac{m_j}{m_j + m_{\ell}} \right) \Omega_{j\ell}^{(1,1)}$$

$$+ \frac{1}{3kT} \sum_{\ell} c_{\ell} (\delta_{ji} - \delta_{i\ell}) \left[\frac{m_{\ell} \mu_{j\ell}}{(m_j + m_{\ell})^2} \right] \left\{ (\Omega_{j\ell}^{(1,3)} - \frac{5}{2} \Omega_{j\ell}^{(1,2)}) - \frac{5}{2} (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)}) \right\}$$

(3.20)

$$D_j \equiv \frac{2}{3kT} \sum_{\ell} c_{\ell} \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) \left\{ \Omega_{j\ell}^{(2,2)} + \frac{15}{4} \left(\frac{m_j - m_{\ell}}{m_{\ell}} \right) \Omega_{j\ell}^{(1,1)} \right\} \quad (3.21)$$

$$E_{ij} \equiv \frac{2}{3kT} \sum_{\ell} c_{\ell} \left\{ \frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i} - c_i (m_j - m_{\ell})}{m_{\ell} + m_j} \right\} \left(\frac{m_{\ell}}{m_{\ell} + m_j} \right) \left(\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)} \right) \quad (3.22)$$

$$F_{ij} \equiv \frac{2}{3kT} \sum_{\ell} c_{\ell} \left\{ \frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i} - c_i (m_j - m_{\ell})}{m_{\ell} + m_j} \right\} \Omega_{\ell j}^{(1,1)} \quad (3.23)$$

Using these definitions we can rewrite equations (3.12), (3.15), and (3.16) as:

$$\sum_j A_{ij} j_j = \sum_j B_{ij} \mathcal{E}_j \quad (3.24)$$

$$d_i^* = 4 \sum_j E_{ij} \mathcal{E}_j - 8 \sum_j F_{ij} j_j \quad (3.25)$$

$$\frac{\partial \ln T}{\partial x} = \frac{16}{5} \sum_j D_j \mathcal{E}_j \quad (3.26)$$

These relations (eqs. (3.24) to (3.26)) are the desired results. j_j is the mass flux of the j 'th species whereas \mathcal{E}_j , which has the dimensions of a mass flux, is a quantity which, when multiplied by the energy per unit mass, corresponds to a conduction heat flux of the j 'th species.

Up to now we have not considered the viscosity. It is, however, convenient to take over the relations needed to calculate the viscosity directly from HCB. From equation (7.4-56) of HCB we may write

$$\eta = \frac{5}{16} \sum_j c_j \gamma_j \quad (3.27)$$

where

$$\gamma_j \equiv \frac{8}{5} \frac{\rho kT}{m_j} b_{jo} \quad (1) \quad (3.28)$$

From equation (7.4-57) of HCB we can write

$$\sum_j G_{ij} \gamma_j = 1 \quad (3.29)$$

where

$$G_{ij} \equiv - \frac{5 m_j}{8 \rho kT} \left(\frac{Q_{ij}^{oo}}{R_{io}} \right)$$

or from equation (7.4-62) of HCB

$$G_{ij} = \frac{5}{16} \frac{m_j n^2}{\rho n_i} H_{ij} \quad (3.30)$$

and substituting equation (7.4-63) of HCB into equation (3.29), yields

$$G_{ij} = \frac{2}{3kT} \sum_l c_l \frac{m_i}{(m_i + m_l)^2} \left\{ 5 m_j (\delta_{ij} - \delta_{jl}) \Omega_{il}^{(1,1)} + \frac{3}{2} m_l (\delta_{ij} + \delta_{jl}) \Omega_{il}^{(2,2)} \right\} \quad (3.31)$$

Equations (3.31), (3.29), and (3.27) now determine the viscosity in terms of the weighted cross sections. The reason we have resorted here to the usual formulation (or a slight modification of it) is because the shear stress is directly proportional to the velocity gradients; hence the velocity gradient can be written as the reciprocal of the viscosity times the shear stress, which is of the same form as equations (3.25) and (3.26). In order to bring the set of equations for the viscosity into the

same form as the set (3.24) through (3.26) for the heat flux and diffusion, it might be more convenient to reformulate the problem to obtain analogous equations to (3.27) and (3.29) for the reciprocal of the viscosity (i.e., equation (3.27) would be replaced by an equation of the form $\frac{1}{\eta} = \sum_j c_j \beta_j$), but at present it does not seem that the additional labor is justified.

The results obtained so far are valid for single temperature monotomic gases only. They are, however, a good approximation for single temperature polyatomic gas mixtures with one exception; that is, equation (3.17) must be modified to take into account the internal motion. In order to accomplish this two things must be done. First, the translation enthalpy of species j , $(\frac{5}{2} \frac{kT}{m_j})$, which multiplies j_j in equation (3.17) must be replaced by the total enthalpy (translational plus internal) of species j and second, a term must be added which takes into account the Eucken correction. This is carried out in Appendix C. We have shown there that the term

$$\frac{1}{2} \sum_j \frac{c_{v, \text{int } j}}{m_j} \mathfrak{E}_j$$

must be added to equation (3.17) in order to bring in the Eucken correction where \mathfrak{E}_j is given by equation (C-9) and (C-10).

If one of the species present is electrons, it might be desirable to take into account the possibility that the electrons are at a different temperature than the rest of the species. This can be accomplished when the isotropic part of the electron distribution function is approximately Maxwellian if the terms of the order of the square root of the

electron-heavy particle mass ratio are neglected in the electron-heavy particle collision integrals. In this case the equation (2.1) for the electrons will involve a different temperature than the heavy particles. Because of the decoupling effect of the mass ratio expansion, however, the solution can be carried out in exactly the same way as was done above.⁹

It can be seen from equation (2.18) that if it is necessary to retain more terms in calculating the collisional effects of say species 1 with itself,* it is only necessary to retain those terms to higher orders in n and r which appear in the terms where i and j are both one. This will bring in additional α_1^n 's, but there will also be an additional algebraic equation for each additional α_1^n . Thus the effect of going to higher order in the polynomial expansion of one of the species is to increase the number of α 's referring to that species and to increase the number of equations by the same amount.

*This corresponds to retaining higher-order terms in the polynomial expansions in the Chapman-Enskog procedures when evaluating say the electron-electron collision integrals.

IV. THE BOUNDARY LAYER PROBLEM

We shall now proceed to formulate the complete boundary layer problem using the relations which were derived above. To these linear algebraic equations and the first-order differential equations, we now must add the conservation equations to get a complete set. We shall rewrite the conservation equations in the form of a set of first-order differential equations in the coordinate normal to the flow. The terms on the right side of these equations will involve a convective derivative. In the cases where similarity solutions exist, this convective derivative becomes a first-order derivative in the similarity variable. These derivatives appearing on the right-hand side can then be eliminated by using the flux equations. This procedure is illustrated by considering a specific example--the stagnation point boundary layer. The procedure would be the same for any similarity boundary layer.

In cases where no similarity solutions exist, it may be desired to expand the solutions to the boundary layer equations in a power series in the coordinate in the direction of flow. If this is done the convective terms on the right will again yield first-order derivatives in the coordinate normal to the flow which can be eliminated as in the case for similarity solutions. Thus in both cases we obtain sets of linear algebraic equations and first-order differential equations with each differential equation containing only one derivative.

In this formulation the effects of chemical reactions and internal molecular structure will be taken into account in the usual approximate way; that is, we shall add to the continuity equation a source term ω_i where:

$$\frac{\omega_i}{m_i} = \left(\frac{Dn_i}{Dt} \right)_{\text{chem. react.}} \quad (4.1)$$

and replace the translational Enthalpy $\frac{5}{2} \frac{kT}{m_i}$ of the i'th species by h_i , the translational plus internal enthalpy of the i'th species, in the appropriate places.

The total enthalpy of all species h is then given by:

$$h = \sum_i c_i h_i \quad (4.2)$$

Then under the boundary layer approximation:

$$\hat{j}_i = \hat{j} j_i, \quad \hat{p}_i = \hat{j} p_i, \quad \underline{q} = \hat{j} q, \quad \underline{y}_0 = \hat{i} u + \hat{j} v \quad (4.3)$$

where \hat{i} is a unit vector in the x-direction and \hat{j} is the unit vector in the y-direction; where x is in the direction of flow and y is perpendicular to the boundary. \underline{d}_i , which is defined by equation (7.3-26) of HCB, now becomes:

$$\underline{d}_i = \hat{j} \frac{\partial}{\partial y} \left(\frac{n_i}{n} \right),$$

and, therefore, from equation (3.14), we have:

$$\begin{aligned} \underline{d}_i^* &= \hat{j} \frac{n}{\rho} \left\{ m_i \frac{\partial}{\partial y} \left(\frac{n_i}{n} \right) - c_i \sum_j m_j \frac{\partial}{\partial y} \left(\frac{n_j}{n} \right) \right\} \\ &= \hat{j} \frac{n}{\rho} \left\{ \frac{\partial}{\partial y} \left(c_i \frac{\rho}{n} \right) - c_i \frac{\partial}{\partial y} \left(\frac{\rho}{n} \right) \right\} \\ &= \hat{j} \frac{\partial}{\partial y} c_i. \end{aligned} \quad (4.4)$$

Using the results of Appendix C (Eq. C-11), equation (3.17) can be written as

$$-q = \frac{5}{4} kT \sum_j \frac{1}{m_j} \mathcal{F}_j - \sum_j h_j j_j + \frac{1}{2} \sum_j \frac{c_{v, \text{int}}}{m_j} j \epsilon_j \quad (4.5)$$

where ϵ_j is given by equations (C-9) and (C-10).

Since $p = nkT$ and

$$\frac{n}{\rho} = \sum_i \frac{c_i}{m_i}, \text{ we have}$$

$$\frac{p}{T\rho} = \sum_i \frac{k}{m_i} c_i \quad (4.6)$$

Now using equations (3.24) through (3.26), (3.27), and (3.29) and equation (3.18), we can write down the boundary layer equations as follows:*

$$\frac{\partial v}{\partial y} = -r \frac{\delta \mathcal{J}(r\delta u)}{\partial x} - \frac{1}{\rho} \frac{D\rho}{Dt} \quad \delta = 0, 1 \quad (4.7)$$

$$\frac{\partial \tau}{\partial y} = -\frac{dp}{dx} - \rho \frac{Du}{Dt} \quad (4.8)$$

$$\frac{\partial(-q)}{\partial y} = -\frac{1}{\eta} \tau^2 + \rho \frac{Dp}{Dt} \quad (4.9)$$

$$\frac{\partial j_i}{\partial y} = \omega_i - \rho \frac{Dc_i}{Dt} \quad (4.10)$$

$$\frac{\partial u}{\partial y} = -\frac{1}{\eta} \tau \quad (4.11)$$

$$\frac{\partial c_i}{\partial y} = 4 \sum_j E_{ij} \mathcal{F}_j - 8 \sum_j F_{ij} j_j \quad (4.12)$$

*Equations (4.7) through (4.10) are merely the conservation equations simplified by the boundary layer approximations, and equation (4.11) is the relation between the shear stress and velocity gradient in the boundary layer. See, for example, reference 10.

$$\frac{\partial T}{\partial y} = \frac{16}{5} T \sum_j D_j \xi_j \quad (4.13)$$

$$-q = \frac{1}{2} \sum_j \left(\frac{5}{2} \frac{kT}{m_j} \right) \xi_j - \sum_j h_j j_j + \frac{1}{2} \sum_j \frac{c_{v, int}}{m_j} j_j \epsilon_j \quad (4.14)$$

$$\eta = \frac{5}{16} \sum_j c_j \gamma_j \quad (4.15)$$

$$h = \sum_j c_j h_j \quad (4.16)$$

$$P = r T \sum_i \frac{k}{m_i} c_i \quad (4.17)$$

$$1 = \sum_i c_i \quad (4.18)$$

$$1 = \sum_j G_{ij} \gamma_j \quad (4.19)$$

$$\sum_j A_{ij} j_j = \sum_j B_{ij} \xi_j \quad (4.20)$$

$$H_j \epsilon_j = \frac{16}{5} T \sum_j D_j \xi_j \quad (4.21)$$

where r is the distance from the center line to the inner edge of the boundary layer in axisymmetric problems, and δ equals one for axisymmetric flow and zero for plane flow. Equations (4.7) through (4.11) are just the usual boundary layer equations. The new relations are given by equations (4.12) through (4.15) and (4.19) and (4.20). For convenience we have listed the definitions of the matrix elements A_{ij} , B_{ij} , D_j , E_{ij} , F_{ij} , G_{ij} , and H_j in Table 1.

TABLE I

Definition of Matrix Elements

$$A_{ij} = \frac{2}{3kT} \sum_{\ell} c_{\ell} (\delta_{ji} - \delta_{\ell i}) \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)})$$

$$B_{ij} = \frac{2}{3kT} \sum_{\ell} c_{\ell} \left\{ \frac{\delta_{ji} m_j + \delta_{i\ell} m_{\ell} - c_i (m_j + m_{\ell})}{m_j + m_{\ell}} \right\} \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) \Omega_{j\ell}^{(2,2)}$$

$$+ \frac{5}{2kT} \sum_{\ell} c_{\ell} \left\{ \frac{\delta_{ji} m_j^2 - \delta_{i\ell} m_{\ell}^2 - c_i (m_j^2 - m_{\ell}^2)}{(m_j + m_{\ell})^2} \right\} \left(\frac{m_j}{m_j + m_{\ell}} \right) \Omega_{j\ell}^{(1,1)}$$

$$+ \frac{1}{3kT} \sum_{\ell} c_{\ell} (\delta_{ji} - \delta_{i\ell}) \left[\frac{m_{\ell} \mu_{j\ell}}{(m_j + m_{\ell})^2} \right] \left\{ (\Omega_{j\ell}^{(1,3)} - \frac{5}{2} \Omega_{j\ell}^{(1,2)}) - \frac{5}{2} (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)}) \right\}$$

$$D_j = \frac{2}{3kT} \sum_{\ell} c_{\ell} \left(\frac{\mu_{j\ell}}{m_j + m_{\ell}} \right) \left\{ \Omega_{j\ell}^{(2,2)} + \frac{15}{4} \left(\frac{m_j - m_{\ell}}{m_{\ell}} \right) \Omega_{j\ell}^{(1,1)} \right\}$$

$$E_{ij} = \frac{2}{3kT} \sum_{\ell} c_{\ell} \left\{ \frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i} - c_i (m_j - m_{\ell})}{m_{\ell} + m_j} \right\} \left(\frac{m_{\ell}}{m_{\ell} + m_j} \right) (\Omega_{j\ell}^{(1,2)} - \frac{5}{2} \Omega_{j\ell}^{(1,1)})$$

$$F_{ij} = \frac{2}{3kT} \sum_{\ell} c_{\ell} \left\{ \frac{m_j \delta_{ji} - m_{\ell} \delta_{\ell i} - c_i (m_j - m_{\ell})}{m_{\ell} + m_j} \right\} \Omega_{\ell j}^{(1,1)}$$

$$G_{ij} = \frac{2}{3kT} \sum_{\ell} c_{\ell} \frac{m_i}{(m_i + m_{\ell})^2} \left\{ 5 m_j (\delta_{ij} - \delta_{j\ell}) \Omega_{i\ell}^{(1,1)} + \frac{3}{2} m_{\ell} (\delta_{ij} + \delta_{j\ell}) \Omega_{i\ell}^{(2,2)} \right\}$$

$$H_j = \frac{8}{3kT} \sum_{\ell} \frac{m_j}{m_{\ell} + m_j} \frac{c_{\ell}}{c_j} \Omega_{ij}^{(1,1)}$$

We now consider a special case of equations (4.7) through (4.18) for the stagnation point. Let the subscript s refer to the free stream conditions. We have

$$u_s = ax$$

$$c_{is} = \text{const.}$$

$$T_s = \text{const.}$$

For this problem there exists a similarity variable η given by

$$\eta = \left[\frac{(1 + \delta)a}{b_o} \right]^{\frac{1}{2}} \int_0^y \rho dy$$

where b_o is some constant reference quantity. In order to use the accepted nomenclature, we shall use η (which has previously been used for the viscosity) as the similarity variable, and we shall designate the viscosity by λ .

We have from the total continuity and momentum equations (4.7) and (5.7)

$$\frac{u}{u_s} = f'(\eta) \quad (4.22)$$

$$v = -\frac{1}{\rho} \left[(\delta + 1) a b_o \right]^{\frac{1}{2}} f(\eta) \quad (4.23)$$

$$\frac{dP}{d\eta} = \frac{1}{(1 + \delta)} \left(\frac{\rho_s}{\rho} - [f']^2 \right) - \frac{b_o}{\lambda \rho} P \quad (4.24)$$

$$\frac{df}{d\eta} = f' \quad (4.25)$$

$$\frac{df'}{d\eta} = -\frac{b_o}{\lambda \rho} P \quad (4.26)$$

also

$$\frac{\partial}{\partial y} = \left[\frac{(1 + \delta) a}{b_0} \right]^{\frac{1}{2}} \rho \frac{d}{d\eta}, \quad (4.27)$$

and for all equations after (4.2), we have

$$\rho \frac{D}{Dt} = -\rho(1 + \delta) a f \frac{d}{d\eta}. \quad (4.28)$$

Equations (4.9) and (4.10) become

$$\frac{d(-q)}{d\eta} = - \left[b_0 a(1 + \delta) \right]^{\frac{1}{2}} f \frac{dh}{d\eta} \quad (4.29)$$

$$\frac{dj_i}{d\eta} = \frac{\omega_i}{\rho} \left[\frac{(1 + \delta) a}{b_0} \right]^{-\frac{1}{2}} + \left[b_0 a(1 + \delta) \right]^{\frac{1}{2}} f \frac{dc_i}{d\eta}, \quad (4.30)$$

but

$$\frac{dh}{d\eta} = \sum_i h_i \frac{dc_i}{d\eta} + \sum_i c_i \frac{dh_i}{dT} \frac{dT}{d\eta},$$

and the specific heat of the i 'th species c_{pi} is given by $c_{pi} = \frac{dh_i}{dT}$.

The total specific heat is c_p is

$$c_p = \sum_i c_i c_{pi},$$

hence

$$\frac{dh}{d\eta} = \sum_i h_i \frac{dc_i}{d\eta} + c_p \frac{dT}{d\eta}. \quad (4.31)$$

Equations (4.12) and (4.13) become

$$\frac{\partial c_i}{\partial \eta} = \left[\frac{b_0}{(1 + \delta) a} \right]^{\frac{1}{2}} \frac{1}{\rho} \left\{ 4 \sum_j E_{ij} \xi_j - 8 \sum_j F_{ij} j_j \right\} \quad (4.32)$$

and

$$\frac{dT}{d\eta} = \frac{16}{5} T \left[\frac{b_o}{(1+\delta)a} \right]^{\frac{1}{2}} \frac{1}{\rho} \sum_j D_j \epsilon_j. \quad (4.33)$$

Substituting (4.33) and (4.32) into (4.31) and then substituting this into (4.29), we get:

$$\begin{aligned} \frac{d(-q)}{d\eta} = \frac{8b_o}{\rho} & \left[\sum_i \sum_j F_{ij} h_i j_j - \frac{1}{2} \sum_i \sum_j E_{ij} h_i \epsilon_j \right. \\ & \left. - \frac{2c_p T}{5} \sum_j D_j \epsilon_j \right], \end{aligned} \quad (4.34)$$

and substituting equation (4.32) into equation (4.30), we get

$$\frac{dj_i}{d\eta} = \frac{\omega_i}{\rho} \left[\frac{(1+\delta)a}{b_o} \right]^{\frac{1}{2}} + \frac{b_o^4}{\rho} \left[\sum_j E_{ij} \epsilon_j - 2 \sum_j F_{ij} j_j \right]. \quad (4.35)$$

Let us define q^+ , j_i^+ , ϵ_i^+ , and λ_i^+ by

$$q^+ \equiv -q / \left[a(1+\delta) b_o \right]^{\frac{1}{2}} \quad (4.36)$$

$$j_i^+ \equiv j_i / \left[a(1+\delta) b_o \right]^{\frac{1}{2}} \quad (4.37)$$

$$\epsilon_i^+ \equiv \epsilon_i / \left[a(1+\delta) b_o \right]^{\frac{1}{2}} \quad (4.38)$$

$$\lambda_i^+ \equiv \lambda_i / \left[a(1+\delta) b_o \right]^{\frac{1}{2}},$$

and we have upon collecting the results

$$\frac{dP}{d\eta} = \frac{1}{(1+\delta)} \left[\frac{\rho s}{\rho} - (f')^2 \right] - \frac{b_o}{\lambda \rho} f P \quad (4.39)$$

$$\frac{df}{d\eta} = f' \quad (4.40)$$

$$\frac{df'}{d\eta} = -\frac{b_o}{\lambda \rho} p \quad (4.41)$$

$$\frac{dq^+}{d\eta} = 8\left(\frac{b_o}{\rho}\right) f \left[\sum_i \sum_j F_{ij} h_i j_j^+ - \frac{1}{2} \sum_i \sum_j E_{ij} h_i \xi_j^+ - \frac{2c_p T}{5} \sum_j D_j \xi_j^+ \right] \quad (4.42)$$

$$\frac{dj_i^+}{d\eta} = \frac{\omega_i}{b_o \rho} + 4\left(\frac{b_o}{\rho}\right) f \left[\sum_j E_{ij} \xi_j^+ - 2 \sum_j F_{ij} j_j^+ \right] \quad (4.43)$$

$$\frac{dc_i}{d\eta} = 4\left(\frac{b_o}{\rho}\right) \left[\sum_j E_{ij} \xi_j^+ - 2 \sum_j F_{ij} j_j^+ \right] \quad (4.44)$$

$$\frac{dT}{d\eta} = \frac{16}{5} T \left(\frac{b_o}{\rho}\right) \sum_j D_j \xi_j^+ \quad (4.45)$$

$$q^+ = \frac{1}{2} \sum_j \left(\frac{5}{2} \frac{kT}{m_j}\right) \xi_j^+ - \sum_j h_j j_j^+ + \frac{1}{2} \sum_j \left(\frac{c_{v,int}}{m_j}\right)_j \xi_j^+ \quad (4.46)$$

$$\lambda = \frac{5}{16} \sum_j c_j \gamma_j \quad (4.47)$$

$$h = \sum_j c_j h_j \quad (4.48)$$

$$p_s = \rho T \sum_i \frac{k}{m_i} c_i \quad (4.49)$$

$$1 = \sum_i c_i \quad (4.50)$$

$$1 = \sum_j G_{ij} \gamma_j \quad (4.51)$$

$$\sum_j A_{ij} j_j^+ = \sum_j B_{ij} \xi_j^+ \quad (4.52)$$

$$H_j \epsilon_j^+ = \frac{16}{5} T \sum_j D_j \xi_j^+ \quad (4.53)$$

For the frozen boundary layer we set $\omega_i = 0$ in equation (4.43). For the equilibrium boundary layer $c_i = c_i(T)$ only. Hence the left-hand side of equation (4.44) can be written as:

$$\frac{dc_i}{dT} \frac{dT}{d\eta}$$

$\frac{dT}{d\eta}$ can then be eliminated between equations (4.44) and (4.45). The result is a set of linear algebraic equations in ξ_i^+ and j_i^+ . After doing this equation (4.43) can be dropped.

V. SUMMARY

In this report a modification to the usual Chapman-Enskog procedure for obtaining normal solutions to the Boltzmann equation has been developed in order to obtain relations between the fluxes appearing in the conservation equations and the gradients of the physical quantities which are in a more convenient form for numerical boundary layer calculations involving many species than those that would be obtained by the usual procedures. The results of this modified Chapman-Enskog procedure are given by equations (3.20) through (3.26) with equation (3.17). These results are then combined with the conservation laws in Part IV and applied to the boundary layer problem. The resulting set of boundary layer equations (eqs. 4.7 through 4.21 with the definitions of Table I) can be seen to consist of first-order differential equations plus a set algebraic equations which are linear in the fluxes. This is a convenient form for numerical calculations. When the equations are applied to a boundary layer for which a similarity variable exists (eqs. (4.39) through (4.53)), the differential equations become ordinary differential equations, and the formulation becomes particularly suited for numerical calculations (which would involve only integration plus matrix inversion).

VI. ACKNOWLEDGMENT

The author wishes particularly to thank J. A. Fay for his helpful criticism and guidance. Thanks are also due to P. Sockol for his discussion of the problem and to C. S. Su for reading and commenting on the manuscript.

APPENDIX A

We shall now prove that

$$I_{ij} \begin{pmatrix} r & n \\ i & j \end{pmatrix} = \frac{1}{3} U \left[s^n(w_j^2) w_j, s^r(w_i^2) w_i \right]_{ij} \quad (A-1)$$

and

$$I_{ij} \begin{pmatrix} r & n \\ i & i \end{pmatrix} = \frac{1}{3} U \left[s^r(w_i^2) w_i, s^n(w_i^2) w_i \right]_{ij} \quad (A-2)$$

Much of the transformation used follows chapter 9 of Chapman and Cowling² closely, and most of the notation is taken from there.

From equation 10, section 4.4 of Chapman and Cowling, it is easily verified that

$$I_{ij} \begin{pmatrix} r & n \\ i & j \end{pmatrix} = I_{ij} \begin{pmatrix} n & r \\ j & i \end{pmatrix} . \quad (A-3)$$

By definition the n'th Sonine Polynomial of order 3/2 is the coefficient of t^n in the expansion of:*

$$(1 - t)^{-5/2} e^{-xt/(1-t)}$$

or:

$$(1 - t)^{-5/2} e^{-w_j^2 t/(1-t)} = \sum_{n=0} s^n(w_j^2) t^n , \quad (A-4)$$

and

$$\begin{aligned} (1 - \ell)^{-5/2} \left[w_i e^{-w_i^2 \ell/(1-\ell)} - w_i' e^{-w_i'^2 \ell/(1-\ell)} \right] \\ = \sum_{r=0} \left[w_i s^r(w_i^2) - w_i' s^r(w_i'^2) \right] \ell^r , \end{aligned}$$

*C. F. Chapman & Cowling² Section 7.5

and upon setting $\tau \equiv t/(1-t)$, $S \equiv \mathcal{L}/(1-\mathcal{L})$, we have:

$$\begin{aligned} & (1-\mathcal{L})^{-5/2} (1-t)^{-5/2} \frac{1}{n_i n_j} \iiint f_i^{(0)} f_j^{(0)} \underline{w}_j e^{-w_j^2} (\underline{w}_i e^{-w_i^2} S - \\ & \quad - \underline{w}_i' e^{-w_i'^2}) g_{ij} \, b \, db \, d\epsilon \, d\underline{v}_i \, d\underline{v}_j \\ & = \sum_{n,r} \underline{I}_{ij} \binom{n}{j} \binom{r}{i} \mathcal{L}^r t^n \end{aligned} \quad (A-5)$$

From equation (6) of Section 3.41 in Chapman and Cowling, we have

$$\underline{C}_i = \underline{G}_{ij} - M_j \underline{g}_{ji}, \quad \underline{C}_j = \underline{G}_{ij} + M_i \underline{g}_{ji}$$

where: $M_i \equiv m_i/(m_i + m_j)$; $M_j = m_j/(m_i + m_j)$

$$(m_i + m_j) \underline{G}_{ij} \equiv m_i \underline{C}_i + m_j \underline{C}_j = m_i \underline{C}_i' + m_j \underline{C}_j',$$

and \underline{C}_i is the velocity of a molecule of species i ; defining \underline{G}_0 by

$$\underline{G}_0 \equiv \underline{G}_{ij} - \underline{v}_0,$$

we have

$$\underline{v}_i = \underline{G}_0 - M_j \underline{g}_{ji}; \quad \underline{v}_j = \underline{G}_0 + M_i \underline{g}_{ji}$$

$$\frac{\partial (\underline{G}_0, \underline{g}_{ji})}{\partial (\underline{v}_i, \underline{v}_j)} = 1; \quad \frac{1}{2} m_i v_i^2 + \frac{1}{2} m_j v_j^2 = \frac{1}{2} (G_0^2 + M_i M_j g_{ij}^2).$$

Next we define

$$\begin{aligned} \underline{g}_0 &= \sqrt{\frac{m_i + m_j}{2 kT}} \underline{G}_0, \quad \underline{g} \equiv \sqrt{\frac{m_i m_j}{m_i + m_j} \cdot \frac{1}{2kT}} \underline{g}_{ji} \\ \underline{g}' &\equiv \sqrt{\frac{m_i m_j}{m_i + m_j} \cdot \frac{1}{2kT}} \underline{g}_{ji}' \end{aligned}$$

and we have*

$$W_i = M_i^{1/2} \underline{g}_o - M_j^{1/2} \underline{g}, \quad W_j = M_j^{1/2} \underline{g}_o + M_i^{1/2} \underline{g},$$

$$W_i' = M_i^{1/2} \underline{g}_o - M_j^{1/2} \underline{g}', \quad ,$$

$$W_i^2 + W_j^2 = \underline{g}_o^2 + \underline{g}^2, \quad ,$$

$$\frac{\partial (\underline{g}_o, \underline{g})}{\partial (\underline{v}_i, \underline{v}_j)} = \frac{(m_i m_j)^{3/2}}{(2kT)^3}, \quad ,$$

and

$$\underline{g} \cdot \underline{g}' = \underline{g}^2 \cos \chi \quad (A-6)$$

where χ is the deflection angle of the relative velocity in an encounter. Any function of the velocities of two molecules after encounter may be transformed into the corresponding function of the velocities before encounter by taking $\chi = 0$, (c.f. Chapman and Cowling, p. 152, Section 9.3, equation 10 and below).

From equation (7.3-13) of HCB we have

$$f_i^{(0)} = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} e^{-W_i^2}.$$

Using the above definitions and relations in equation (A-5), we get

$$\begin{aligned} \sum_{n,r} I_{ij} \binom{n}{j} \binom{r}{i} \int \dots \int &= \\ (1 - \int)^{-5/2} (1 - t)^{-5/2} \pi^{-3} \iiint & e^{-W_i^2 - W_j^2} \underline{W}_j e^{-W_j^2} \tau (W_i e^{-W_i^2} \underline{W}_i' e^{-W_i'^2} S) \times \\ \times g_{ij} b db d\epsilon d\underline{g} d\underline{g}_o & \end{aligned}$$

* c.f. equation 7, Section 3.41 of Chapman and Cowling⁽²⁾

$$\begin{aligned}
 &= (1 - f)^{-5/2} (1 - t)^{-5/2} \pi^{-3} \iiint e^{-\mathcal{L}_0^2 - \gamma^2} \left[e^{-W_j^2 \tau - W_i^2 s} \underline{W}_j \underline{W}_i - \right. \\
 &\quad \left. - \underline{W}_j \underline{W}_i' e^{-W_j^2 \tau - W_i'^2 s} \right] g_{ij} \, bd \, bd \epsilon \, d\gamma \, dG_0 \\
 &= (1 - f)^{-5/2} (1 - t)^{-5/2} \pi^{-3} \iint \left[\underline{H}_{ij}(0) - \underline{H}_{ij}(\chi) \right] g_{ij} \, bd \, bd \gamma. \quad (A-7)
 \end{aligned}$$

Where

$$\underline{H}_{ij}(\chi) = \iiint \left\{ \exp \left[-\mathcal{L}_0^2 - \gamma^2 - W_j^2 \tau - W_i'^2 s \right] \right\} \underline{W}_j \underline{W}_i' \, d\mathcal{L}_0 \, d\epsilon \quad (A-8)$$

$$\underline{H}_{ij}(0) = \iiint \left\{ \exp \left[-\mathcal{L}_0^2 - \gamma^2 - W_j^2 \tau - W_i^2 s \right] \right\} \underline{W}_j \underline{W}_i \, d\mathcal{L}_0 \, d\epsilon \quad (A-9)$$

We now have

$$W_j^2 = (M_i^{1/2} \mathcal{L}_0 + M_i^{1/2} \gamma) \cdot (M_j^{1/2} \mathcal{L}_0 + M_j^{1/2} \gamma)$$

$$= M_j \mathcal{L}_0^2 + M_i \gamma^2 + 2(M_i M_j)^{1/2} \mathcal{L}_0 \cdot \gamma$$

$$W_i'^2 = M_i \mathcal{L}_0^2 + M_j \gamma^2 - 2(M_i M_j)^{1/2} \mathcal{L}_0 \cdot \gamma'$$

Hence

$$\mathcal{L}_0^2 + \gamma^2 - s W_i'^2 + \tau W_j^2 = i_{ij} \mathcal{L}_0^2 + i_{ji} \gamma^2 + 2(M_i M_j)^{1/2} (\tau \mathcal{L}_0 \cdot \gamma - s \mathcal{L}_0 \cdot \gamma').$$

Where

$$i_{ij} \equiv 1 + M_i S + M_j \tau$$

$$i_{ji} \equiv 1 + M_j S + M_i \tau .$$

Let

$$\mathcal{V} = \mathcal{L}_0 + \frac{1}{i_{ij}} (M_i M_j)^{1/2} (\tau \mathcal{X} - S \mathcal{X}')$$

so that a variable change from \mathcal{L}_0 to \mathcal{V} is equivalent to a change in origin in the \mathcal{L}_0 space.

$$\mathcal{L}_0^2 + \mathcal{Y}^2 + S W_i'^2 + \tau W_j^2 = i_{ij} \mathcal{V}^2 + i_{ji} \mathcal{Y}^2 -$$

$$- (M_i M_j / i_{ij}) (\tau \mathcal{X} - S \mathcal{X}') \cdot (\tau \mathcal{X} - S \mathcal{X}') = i_{ij} \mathcal{V}^2 + j_{ij} \mathcal{Y}^2$$

where

$$j_{ij} \equiv i_{ji} - (M_i M_j / i_{ij}) (S^2 + \tau^2 - 2 S \tau \cos \chi)$$

$$= 1 + M_j S + M_i \tau - \frac{M_i M_j (S^2 + \tau^2 - 2 S \tau \cos \chi)}{1 + M_i S + M_j \tau}$$

$$= \frac{(1 + S)(1 + \tau) - 2 M_i M_j S \tau (1 - \cos \chi)}{1 + M_i S + M_j \tau}$$

$$= \left\{ 1 - 2 M_i M_j S \tau (1 - \cos \chi) \right\} / (1 - M_j S - M_i \tau) ,$$

or

$$j_{ij} = \left\{ 1 - 2 M_i M_j S \tau (1 - \cos \chi) \right\} / (1 - M_j S - M_i \tau) .$$

Let

$$\underline{v}_i \equiv (M_i/i_{ij})(\tau \underline{v} - S \underline{v}') + \underline{v}'$$

$$\underline{v}_j \equiv (M_j/i_{ij})(\tau \underline{v} - S \underline{v}') - \underline{v}$$

then

$$\underline{w}_i' = M_i^{1/2} \underline{v} - M_j^{1/2} \underline{v}_i$$

$$\underline{w}_j = M_j^{1/2} \underline{v} - M_i^{1/2} \underline{v}_j$$

$$\underline{w}_i' \underline{w}_j = (M_i M_j)^{1/2} \underline{v} \underline{v}$$

$$- \underline{v} (M_j \underline{v}_i + M_i \underline{v}_j) + (M_i M_j)^{1/2} \underline{v}_i \underline{v}_j$$

$$\underline{w}_i'^2 = M_i \underline{v}^2 - 2(M_i M_j)^{1/2} \underline{v} \cdot \underline{v}_i + M_i \underline{v}_i^2$$

$$\underline{w}_j^2 = M_j \underline{v}^2 - 2(M_i M_j)^{1/2} \underline{v} \cdot \underline{v}_j + M_j \underline{v}_j^2$$

$$\underline{v}_o^2 + \gamma^2 + S \underline{w}_i'^2 + \tau \underline{w}_j^2 = i_{ij} \underline{v}^2 + i_{ji} \gamma^2$$

$$- (M_i M_j / i_{ij}) (\tau \underline{v} - S \underline{v}') \cdot (\tau \underline{v} - S \underline{v}')$$

$$= i_{ij} \underline{v}^2 + j_{ij} \gamma^2.$$

Then by equation 2 of Section 1.42 in Chapman and Cowling, equation (A-8) can be rewritten in terms of these new variables as

$$\begin{aligned}
 \underline{H}_{ij}(\chi) &= (M_i M_j)^{1/2} \int \left[\exp.(-i_{ij} \underline{r}^2 - j_{ij} \chi^2) \right] (\underline{r} \underline{r} + \underline{r}_i \underline{r}_j) d\underline{r} d\epsilon \\
 &= 4\pi (M_i M_j)^{1/2} \iint_0^\infty \left[\exp.(-i_{ij} \underline{r}^2 - j_{ij} \chi^2) \right] \left(\frac{1}{3} \underline{U} \underline{r}^2 + \underline{r}_i \underline{r}_j \right) \underline{r}^2 d\underline{r} d\epsilon \\
 &= \pi^{3/2} (M_i M_j)^{1/2} \int e^{-j_{ij} \chi^2} (i_{ij})^{-5/2} \left(\frac{3}{2} \frac{1}{3} \underline{U} + i_{ij} \underline{r}_i \underline{r}_j \right) d\epsilon. \quad (A-10)
 \end{aligned}$$

since $\underline{r}_i \underline{r}$ and $\underline{r}_j \underline{r}$ are odd functions of \underline{r} , and $\underline{r} \underline{r}$ is an even function and \underline{U} is the unit tensor.

$$\begin{aligned}
 \underline{r}_i \underline{r}_j &= (M_i M_j / i_{ij}^2) (\tau \underline{r} - S \underline{r}') (\tau \underline{r} - S \underline{r}') \\
 &\quad + (1/i_{ij}) (M_j \underline{r}' - M_i \underline{r}) (\tau \underline{r} - S \underline{r}') - \underline{r} \underline{r}' \\
 &= (M_i M_j / i_{ij}^2) (\tau^2 \underline{r} \underline{r} + S^2 \underline{r}' \underline{r}' - 2 S \tau \underline{r} \underline{r}') \\
 &\quad + (1/i_{ij}) \left\{ -M_i \tau \underline{r} \underline{r} - M_j S \underline{r}' \underline{r}' + (M_i S + M_j \tau) \underline{r} \underline{r}' \right\} - \underline{r} \underline{r}' \quad (A-11)
 \end{aligned}$$

Let \underline{K} be the unit vector in the plane of \underline{g}_{ji} and \underline{g}'_{ji} which is perpendicular to \underline{g}_{ji} ; then we have

$$\begin{aligned}
 \underline{r} \cdot \underline{r}' &= r^2 \cos \chi \\
 \underline{r} \times \underline{r}' &= \underline{K} r^2 \sin \chi
 \end{aligned}$$

and $\underline{K} = \underline{K}(\underline{r}, \epsilon)$ only, since once ϵ , \underline{g}_{ji} are specified, \underline{K} is completely determined.

Now we have

$$\underline{r}' = \underline{r} \cos \chi + \underline{K} r \sin \chi, \quad (A-12)$$

hence

$$\underline{\gamma} \underline{\gamma}' = \underline{\gamma} \underline{\gamma} \cos \chi + \underline{\gamma} \underline{K} \underline{\gamma} \sin \chi \quad (\text{A-13})$$

$$\begin{aligned} \underline{\gamma}' \underline{\gamma}' &= \underline{\gamma} \underline{\gamma} \cos^2 \chi + \underline{K} \underline{K} \underline{\gamma}^2 \sin^2 \chi \\ &+ 2 \underline{\gamma} \underline{K} \underline{\gamma} \cos \chi \sin \chi \end{aligned} \quad (\text{A-14})$$

It is easy to see from Figure 1 that

$$\int_0^{2\pi} \underline{K} \underline{K} d\epsilon = 0 \quad (\text{A-15})$$

and that*

$$\int_0^{2\pi} \underline{K} \underline{K} d\epsilon = \frac{1}{2}(\underline{U} - \underline{\gamma} \underline{\gamma} / \underline{\gamma}^2) \int_0^{2\pi} d\epsilon \quad (\text{A-16})$$

We now have from equations (15-a) and (13-a)

$$\int_0^{2\pi} \underline{\gamma} \underline{\gamma}' d\epsilon = \underline{\gamma} \underline{\gamma} \cos \chi \int_0^{2\pi} d\epsilon, \quad (\text{A-17})$$

and from equations (14-a), (15-a), and (16-a)

$$\begin{aligned} \int_0^{2\pi} \underline{\gamma}' \underline{\gamma}' d\epsilon &= [\underline{\gamma} \underline{\gamma} \cos^2 \chi + \frac{1}{2}(\underline{U} \underline{\gamma}^2 - \underline{\gamma} \underline{\gamma}) \sin^2 \chi] \int_0^{2\pi} d\epsilon \\ &= \underline{\gamma} \underline{\gamma} \int_0^{2\pi} d\epsilon - \frac{3}{2} \underline{\gamma} \underline{\gamma}^0 \int_0^{2\pi} d\epsilon \sin^2 \chi \end{aligned} \quad (\text{A-18})$$

where $\underline{\gamma} \underline{\gamma}^0$ is the divergence-less tensor,**

$$\underline{\gamma} \underline{\gamma} - \frac{1}{3} \underline{U} \underline{\gamma}^2.$$

*Note obvious tensor character of $\underline{K} \underline{K}$. The result is essentially obtained by evaluating $\underline{K} \underline{K}$ in a particular coordinate system and then writing it down in an invariant manner.

**in Chapman and Cowling's notation.

From equations (11-a), (17-a), and (18-a), we get

$$\begin{aligned}
 \int_0^{2\pi} \underline{r}_i \underline{r}_j d\epsilon &= \left\{ (M_i M_j / i_{ij}^2) (\tau^2 + S^2 - 2 S \tau \cos \chi) \underline{r}_i \underline{r}_j \right. \\
 &+ (1/i_{ij}) \left[-M_i \tau - M_j S + (M_i S + M_j \tau) \cos \chi \right] \underline{r}_i \underline{r}_j \\
 &- \underline{r}_i \underline{r}_j \cos \chi - \left[S^2 (M_i M_j / i_{ij}^2) - \frac{M_j S}{i_{ij}} \right] \frac{3}{2} \underline{r}_i^0 \underline{r}_j^0 \sin^2 \chi \left. \right\} \int_0^{2\pi} d\epsilon \\
 &= \underline{r}_i \underline{r}_j (1/i_{ij}) \left\{ i_{ji} - j_{ij} - (M_j S + M_i \tau) + \right. \\
 &+ (M_i S + M_j \tau) \cos \chi - i_{ij} \cos \chi \left. \right\} \int_0^{2\pi} d\epsilon \\
 &- 1/i_{ij} \underline{r}_i^0 \underline{r}_j^0 \left\{ \frac{SM_i}{2} - i_{ij} \right\} \frac{SM_j}{i_{ij}} \int_0^{2\pi} d\epsilon \sin^2 \chi \\
 &= \underline{r}_i \underline{r}_j (1/i_{ij}) (1 - j_{ij} - \cos \chi) \int_0^{2\pi} d\epsilon \\
 &+ \frac{3}{2} \underline{r}_i^0 \underline{r}_j^0 \frac{SM_j}{i_{ij}^2} (1 + M_j \tau) \int_0^{2\pi} d\epsilon \sin^2 \chi. \quad (A-19)
 \end{aligned}$$

Hence substituting equation (A-19) into equation (A-10), we arrive at

$$\begin{aligned}
 \underline{H}_{ij}(\chi) &= \pi^{3/2} (M_i M_j)^{1/2} e^{-j_{ij} \chi^2} (i_{ij})^{-5/2} \left\{ \frac{3}{2} \cdot \frac{1}{3} \underline{U} + (1 - j_{ij} - \cos \chi) \underline{r}_i \underline{r}_j \right. \\
 &+ \sin^2 \chi \underline{r}_i^0 \underline{r}_j^0 \frac{SM_i}{i_{ij}} (1 + m_j \tau) \left. \right\} \int_0^{2\pi} d\epsilon. \quad (A-20)
 \end{aligned}$$

From equations (2) and (3) of Section 1.42, p. 22 of Chapman and Cowling, we have

$$\int \underline{\underline{g}}^0 \underline{\underline{g}} \, d\underline{\underline{g}} = 0 \quad (\text{A-21})$$

$$\int \underline{\underline{g}} \underline{\underline{g}} \, d\underline{\underline{g}} = \frac{1}{3} \underline{\underline{U}} \int \underline{\underline{g}}^2 \, d\underline{\underline{g}}. \quad (\text{A-22})$$

Integrating equation (A-20) with respect to $\underline{\underline{g}}$ and using equations (A-21) and (A-22), we get

$$\int \underline{\underline{H}}_{ij} (\underline{\underline{X}}) \, d\underline{\underline{g}} = \frac{1}{3} \underline{\underline{U}} \iint \pi^{3/2} (M_i M_j)^{1/2} e^{-j_{ij} \underline{\underline{g}}^2} (i_{ij})^{-5/2} \left(\frac{3}{2} + [1 - j_{ij} - \cos \underline{\underline{X}}] \underline{\underline{g}}^2 \right) d\underline{\underline{\epsilon}} \, d\underline{\underline{g}}. \quad (\text{A-23})$$

Comparing (A-23) with equation (14) of Section 9.31 of Chapman and Cowling, we see that

$$\int \underline{\underline{H}}_{ij} (\underline{\underline{X}}) \, d\underline{\underline{g}} = \frac{1}{3} \underline{\underline{U}} \iint \underline{\underline{H}}_{ij} (\underline{\underline{X}}) \, d\underline{\underline{\epsilon}} \, d\underline{\underline{g}} \quad (\text{A-24})$$

where $\underline{\underline{H}}_{ij}$ is the H_{12} appearing in Chapman and Cowling, and $\underline{\underline{g}}$ is the script g used there. Also, from the statement appearing below equation (4) of Section 9.31 and the definition of $\underline{\underline{H}}_{12} (0)$ and $\underline{\underline{H}}_{ij} (0)$, we see that

$$\int \underline{\underline{H}}_{ij} (0) \, d\underline{\underline{g}} = \frac{1}{3} \underline{\underline{U}} \iint \underline{\underline{H}}_{ij} (0) \, d\underline{\underline{\epsilon}} \, d\underline{\underline{g}}. \quad (\text{A-25})$$

Using equations (A-24) and (A-25) in equations (A-7) and comparison with* (5) and (2) of Section 9.3 of Chapman and Cowling show that**

* Also see the statement preceding (2).

** Note that our $\underline{\underline{W}}_j$ is Chapman and Cowling's script \mathcal{C}_j .

$$\sum_{n,r} I_{ij} \binom{n}{j} \binom{r}{i} s^r t^n = \frac{1}{3} \sum_{n,r} \left[s^n (w_j^2) w_j, s^r (w_i^2) w_i \right]_{ij} s^r t^n, \quad (A-26)$$

and upon equating coefficients of like powers of s and t , we have

$$I_{ij} \binom{r}{i} \binom{n}{j} = I_{ij} \binom{n}{j} \binom{r}{i} = \frac{1}{3} \sum \left[s^n (w_j^2) w_j, s^r (w_i^2) w_i \right]_{ij} \quad (A-27)$$

which is the first of the desired results. In exactly the same way, we have

$$\begin{aligned} & \sum_{n,r} I_{ij} \binom{n}{i} \binom{r}{j} s^r t^n \\ &= (1-s)^{-5/2} (1-t)^{-5/2} \pi^{-3} \iint \left[H_{ii}(0) - H_{ii}(X) \right] g_{ij} \, d\mathbf{b} \, d\mathbf{b}' \quad (A-28) \end{aligned}$$

where

$$H_{ii}(X) \equiv \int e^{-\frac{1}{2} \mathbf{b}_0^2 - \frac{1}{2} \mathbf{b}'^2 - \frac{1}{2} \mathbf{w}_i^2 \tau - \frac{1}{2} \mathbf{w}_i'^2 s} w_i w_i' d\mathbf{b}_0 d\mathbf{b}' \quad (A-29)$$

and since

$$\begin{aligned} w_i^2 &= M_i \mathbf{b}_0^2 + M_j \mathbf{b}'^2 - 2(M_i M_j)^{1/2} \mathbf{b}_0 \cdot \mathbf{b}' \\ \mathbf{b}_0^2 + \mathbf{b}'^2 + s w_i'^2 + \tau w_i^2 &= i_i \mathbf{b}_0^2 + i_j \mathbf{b}'^2 - \\ &- 2(M_i M_j)^{1/2} (s \mathbf{b}_0 \cdot \mathbf{b}' + \tau \mathbf{b}_0 \cdot \mathbf{b}') \end{aligned}$$

where

$$i_i \equiv 1 + M_i (s + \tau) ; i_j \equiv 1 + M_j (s + \tau) .$$

We find upon setting

$$\mathbf{b} = \mathbf{b}_0 - (M_i M_j)^{1/2} (s \mathbf{b}' + \tau \mathbf{b}) / i_i ; \quad (A-30)$$

following exactly the same procedure as used above and comparing the results with those of Section 9.4 of Chapman and Cowling

$$\underline{I}_{ij} \begin{pmatrix} n & r \\ i & i \end{pmatrix} = \underline{I}_{ij} \begin{pmatrix} r & n \\ i & i \end{pmatrix} = \frac{1}{3} \underline{U} \left[s^r(w_i^2) \underline{w}_i, s^n(w_i^2) \underline{w}_i \right]_{ij} \quad (\text{A-31})$$

APPENDIX B

Calculation of Some Transport Properties for Simple Cases

1. Thermal conductivity of a single-component mixture

Consideration of the quantities defined by (3.19) through (3.23) shows that

$$\left. \begin{aligned} A_{ij} &= A_{11} = 0 \\ B_{ij} &= B_{11} = 0 \\ E_{ij} &= E_{11} = 0 \\ F_{ij} &= F_{11} = 0 \end{aligned} \right\} \quad (B-1)$$

$$D_j = D_1 = \frac{\Omega^{(2,2)}}{6kT} \quad (B-2)$$

From equation (3.26) we have

$$\frac{\partial T}{\partial \underline{r}} = \frac{16}{30} \frac{\Omega^{(2,2)}}{k} \xi_1 \quad (B-3)$$

$$\xi_1 = \frac{30k}{16} \frac{1}{\Omega^{(2,2)}} \frac{\partial T}{\partial \underline{r}} \quad (B-4)$$

From equation (3.17) we have

$$\begin{aligned} g_1 &= -\frac{5}{4} \frac{kT}{m} \xi_1 = -\frac{75}{32} \frac{k^2 T}{m} \frac{1}{\Omega^{(2,2)}} \frac{\partial T}{\partial \underline{r}}, \\ &= -\frac{25}{16} kT \frac{1}{\Omega^{(2,2)}} (C_v/m) \frac{\partial T}{\partial \underline{r}} \end{aligned} \quad (B-5)$$

or introducing the thermal conductivity λ , we have

$$\lambda = \frac{25}{32} \frac{2kT}{\Omega^{(2,2)}} (C_v/m) \quad (B-6)$$

From equation (8.2-8) of HCB we have

$$\Omega^{(2,2)*} \equiv \frac{1}{2} \sqrt{\pi m/kT} \frac{\Omega^{(2,2)}}{\pi \sigma^2}, \quad (B-7)$$

and in terms of this we have

$$\lambda = \frac{25}{32} \frac{\sqrt{\pi m kT}}{\pi \sigma^2 \Omega^{(2,2)*}} (C_v/m) \quad (B-8)$$

which is equation (8.2-11) of HCB for the thermal conductivity of a single-component gas.

2. Binary diffusion coefficient of two-component isothermal mixture

From equations (3.26) and (3.24) and (3.18), we have

$$\left. \begin{aligned} \xi_1 &= \xi_2 = 0 \\ j_1 &= -j_2 \end{aligned} \right\} \quad (B-9)$$

From equation (3.13) we have

$$\begin{aligned} \frac{m_2 n}{\rho} d_2 &= - \frac{16}{3kT} \left\{ j_1 \left(- \frac{c_2 m_2}{m_1 + m_2} \right) \Omega_{21}^{(1,1)} + \right. \\ &+ j_2 \left(\frac{c_1 m_2}{m_1 + m_2} \right) \Omega_{21}^{(1,1)} \\ &= \frac{16}{3kT} \left(\frac{c_2 m_2}{m_1 + m_2} \right) \Omega_{21}^{(1,1)} j_1 (c_1 + c_2) \\ &= \frac{16}{3kT} \left(\frac{2}{m_1 + m_2} \right) n_1 m_1 \Omega_{21}^{(1,1)} \bar{v}_1 \end{aligned}$$

since $c_1 + c_2 = 1$, and $n_1 m_1 \bar{y}_1 \equiv j_1$.

Or

$$\bar{y}_1 = \left(\frac{n m_2}{n_1 \rho} \right) \frac{3kT(m_1 + m_2)}{16 m_1 m_2 \Omega_{21}^{(1,1)}} d_2 \quad (B-10)$$

From equation (7.4-3) of HCB, we have

$$\begin{aligned} \bar{y}_1 &= \frac{n^2}{n_1 \rho} \left[m_1 D_{11} d_1 + m_2 D_{12} d_2 \right] \\ &= \frac{n^2}{n_1 \rho} m_2 D_{12} d_2 \end{aligned} \quad (B-11)$$

since $D_{11} \equiv 0$ (c.f. top p. 487 in HCB).

Comparing equations (B-10) and (B-11), we have

$$D_{12} = \frac{3kT(m_1 + m_2)}{16 n m_1 m_2} \cdot \frac{1}{\Omega_{21}^{(1,1)}} \quad (B-12)$$

which is the same as equation (7.4-38) of HCB for the binary diffusion coefficient of a two-component mixture.

APPENDIX C

Eucken Correction

We have mentioned at the end of Part III that in order to apply the results obtained above to polyatomic gases, it is necessary to add a term to the expression for the heat flux. This can be seen from the results of reference (11) where it is shown that in the "Eucken limit":

$$q - q_{\text{mon}} = - [\lambda_{\text{int.}}]_1 \frac{\partial T}{\partial r} \quad (\text{C-1})$$

where q_{mon} is the heat flux that would be observed if the gas were monatomic and q is the actual heat flux. Hence the term:

$$- [\lambda_{\text{int}}] \frac{\partial T}{\partial r} \quad (\text{C-2})$$

must be added to the expression (3.17) in order to make our results applicable to polyatomic gases.

In order to add this correction term in a way that is in the form of the results derived above, we shall introduce a new set of flux-like quantities, ϵ_j , (related to the flux of internal energy) which are proportional to $\frac{\partial T}{\partial r}$. We shall then use equation (3.26) to eliminate the $\frac{\partial T}{\partial r}$ dependence of the ϵ_j . It is further shown in reference (11) that:

$$[\lambda_{\text{int}}]_1 = \sum_i n_i c_{v_{\text{int}_i}} \left[\sum_j \frac{x_i}{[\epsilon_{ij}]_1} \right]^{-1}, \quad (\text{C-3})$$

and from HCB (eq. 7.4-38), we have

$$[\epsilon_{ij}]_1 = \frac{3 kT}{16 \mu_{ij} n} \frac{1}{\Omega_{ij}(1,1)}. \quad (\text{C-4})$$

Hence

$$[\lambda_{int}]_1 = \sum_i n_i c_{v_{int_i}} \left[\frac{16}{3} \sum_j \frac{\mu_{ij}}{kT} n_j \Omega_{ij}^{(1,1)} \right]^{-1}, \quad (C-5)$$

Let us require that ξ_j satisfy the relation:

$$\frac{1}{2} \sum_i \frac{c_{v_{int_i}}}{m_i} \xi_i = [\lambda_{int}]_1 \frac{\partial T}{\partial \underline{r}} \quad (C-6)$$

$$= \sum_i n_i c_{v_{int_i}} \left[\frac{16}{3} \sum_j \frac{\mu_{ij}}{kT} n_j \Omega_{ij}^{(1,1)} \right]^{-1} \frac{\partial T}{\partial \underline{r}}.$$

This is satisfied by setting

$$\xi_j = \frac{\partial T}{\partial \underline{r}} \left[\frac{8}{3kT} \sum_{\ell} \frac{m_j}{m_{\ell} + m_j} \frac{c_{\ell}}{c_j} \Omega_{\ell j}^{(1,1)} \right]^{-1}, \quad (C-7)$$

and if we define H_j by

$$H_j = \frac{8}{3kT} \sum_{\ell} \frac{m_j}{m_{\ell} + m_j} \frac{c_{\ell}}{c_j} \Omega_{\ell j}^{(1,1)}, \quad (C-8)$$

we have using equation (3.26) to eliminate $\frac{\partial T}{\partial \underline{r}}$ from equation (C-7)

$$H_j \xi_j = \frac{16}{5} T \sum_j D_j \xi_j. \quad (C-9)$$

Hence adding (C-2) to the expression (3.17) and using (C-6), we have

$$-q = \frac{5}{4} kT \sum_j \frac{1}{m_j} \xi_j - \sum_j \left(\frac{5}{2} \frac{kT}{m_j} \right) j_j + \frac{1}{2} \sum_j \frac{c_{v_{int_j}}}{m_j} \xi_j \quad (C-10)$$

Equations (C-8), (C-9), and (C-10) now bring in Eucken correction completely.

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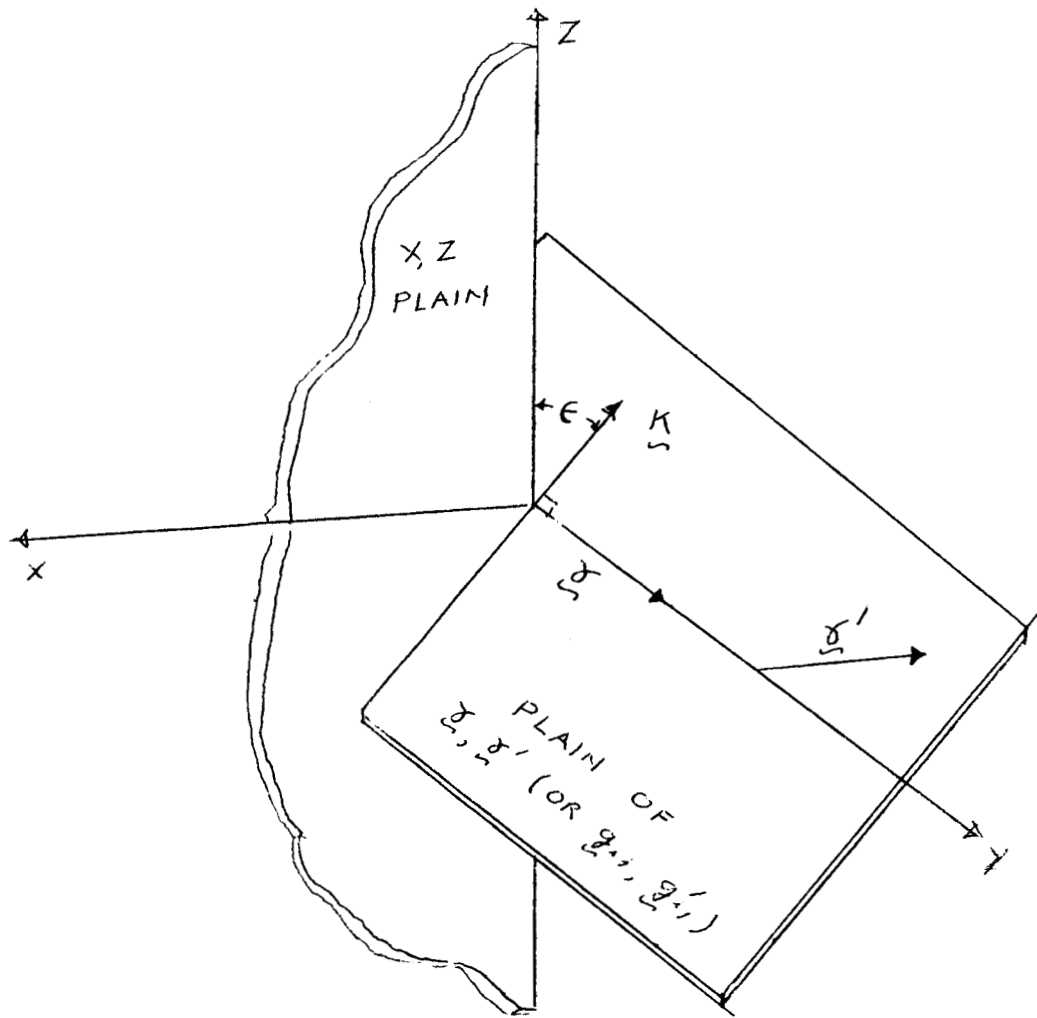


FIGURE 1